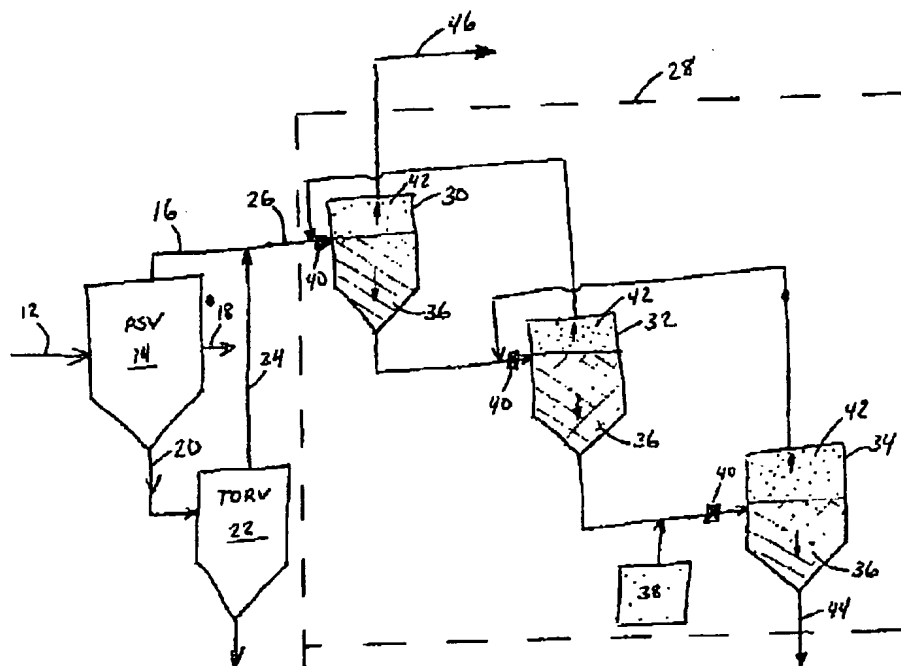




(74) Agent: KIRBY EADES GALE BAKER

(54) Title: ZONE SETTLING AID AND METHOD FOR PRODUCING DRY DILUTED BITUMEN WITH REDUCED LOSSES OF ASPHALTENES



A method includes diluting a bitumen source, such as a bitumen froth from a hot water extraction process, with a hydrocarbon diluent such as naphtha, contacting the bitumen with a zone settling aid such as a polyoxyalkylate block polymer, flocculating water and fine solids in the diluted bitumen, separating the flocculated water and fine solids from the solvent-diluted bitumen, and producing dry, clean diluted bitumen. Preferably, the diluted bitumen will have less than 1.0 wt% water, but most preferably less than 0.7 wt% water. The method may further comprise maintaining the diluted bitumen under conditions that avoid the precipitation of asphaltenes from the bitumen, preferably such that the dry, clean diluted bitumen comprises essentially all, such as greater than 96%, of the asphaltene content from the bitumen source. Counter-current flow may be performed in a series of zone settling stages, such as with gravity settling.

**ABSTRACT**

A method includes diluting a bitumen source, such as a bitumen froth from a hot water extraction process, with a hydrocarbon diluent such as naphtha, contacting the bitumen with a zone settling aid such as a polyoxyalkylate block polymer, flocculating water and fine solids in the diluted bitumen, separating the flocculated water and fine solids from the solvent-diluted bitumen, and producing dry, clean diluted bitumen. Preferably, the diluted bitumen will have less than 1.0 wt% water, but most preferably less than 0.7 wt% water. The method may further comprise maintaining the diluted bitumen under conditions that avoid the precipitation of asphaltenes from the bitumen, preferably such that the dry, clean diluted bitumen comprises essentially all, such as greater than 96%, of the asphaltene content from the bitumen source. Counter-current flow may be performed in a series of zone settling stages, such as with gravity settling.

**ZONE SETTLING AID AND METHOD FOR PRODUCING  
DRY DILUTED BITUMEN WITH REDUCED LOSSES OF ASPHALTENES**

**BACKGROUND OF THE INVENTION**

Field of the Invention

[0001] The present invention relates to compositions and processes for the treatment of bitumen to remove water and solids.

Description of the Related Art

[0002] The Athabasca Oil Sands Deposit is, by itself, the largest petroleum resource in the world. These oil sands or tar sands are located in northwestern Canada and represent the equivalent of roughly 1.6 to 2.7 trillion barrels of oil. Presently, truck and shovel operations first mine the oil sand and deliver it to a crusher. In one process, bitumen separation and recovery from the oil sand is accomplished by following what is known as the Clark hot water extraction process. In the front end of this process, the crushed oil sand is mixed with hot water and caustic in a rotating tumbler or conditioned in a pipeline to produce an aqueous slurry. The slurry is then screened to remove large rocks and the like. The screened slurry is diluted with additional water and the product is then temporarily retained in a primary separation vessel (PSV). In the tumbler, bitumen globules contact and coat air bubbles that are entrained in the slurry. In the PSV, the buoyant bitumen-coated air bubbles rise through the slurry and form bitumen froth. The sand in the slurry settles and is discharged from the base of the vessel, together with some water and bitumen. This stream or portion is referred to as the "PSV underflow" or tailings. A "middlings" portion may also be collected, comprising water, non-buoyant bitumen and fines, from the middle of the PSV. The froth overflows the lip of the vessel and is recovered as the primary froth, typically comprising 60 wt. % bitumen, 30 wt. % water and 10 wt. % particulate solids.

[0003] The PSV underflow is introduced into a deep cone vessel, referred to as the tailings oil recovery vessel ("TORV"). Here the PSV underflow is contacted and mixed with a stream of aerated middlings from the PSV. Again, bitumen and air bubbles contact

and unite to form buoyant globules that rise and form froth. This "secondary" froth overflows the lip of the TORV and is recovered. The secondary froth typically comprises 45 wt. % bitumen, 45 wt. % water and 10 wt. % solids. The middlings from the TORV are withdrawn and processed in a series of sub-aerated, impeller-agitated flotation cells. Secondary froth, typically comprising 40 wt. % bitumen, 50 wt. % water and 10 wt. % solids, is produced from these cells.

[0004] The primary and secondary froth streams are typically combined to yield a product froth stream, often comprising 60 wt. % bitumen, 32 wt. % water and 8 wt. % solids. The water and solids in the froth are contaminants which need to be reduced in concentration before the froth can be treated in a downstream refinery-type upgrading facility. This cleaning operation is carried out using what is referred to as "froth treatment".

[0005] While there are a variety of froth treatment processes, all of these processes include deaeration of the combined froth product followed by dilution with sufficient solvent, specifically naphtha, to provide a solvent to froth ("S/F") ratio of about 0.40 (w/w). This is done to increase the density differential between the diluted bitumen on the one hand and the water and solids on the other.

[0006] Kizior (U.S. Patent 4,383,914) discloses that bitumen froth may be treated in a two-stage dilution centrifuging circuit. The naphtha-diluted bitumen is treated in a battery of scroll separators to remove coarse solids, then pumped through a battery of disc separators to remove water and fine clay solids. In order to obtain a disc product that is acceptable for utilization in downstream bitumen upgrading units, Kizior states that it is conventional to add a chemical demulsifier to the feed stream just before it enters the disc separator. Kizior includes the use of a low shear pump between the first and second stages of centrifugal separation.

[0007] Guymon (U.S. Patent 4,968,412) discloses a process for removal of bitumen from tar sands contaminated with clay, including use of a solvent and centrifugal separation followed by a step of washing residual bitumen with entrapped clay and

solvent from sand using water containing an appropriate surfactant. Guymon discloses that the surfactant may be a primary alcohol ethoxylate, such as a C8 to C15 alcohol with 3 to 8 ethoxylate units. It is stated that greater than eleven ethoxylate units renders the surfactant unusable.

[0008] Graham et al. (U.S. Patent 5,143,598) discloses a deasphalting method of mineral fines removal wherein a bitumen-rich solvent phase containing fines is contacted with a solvent of limited solubility for asphaltenes. A portion of the asphaltene content of the bitumen precipitates and in so doing acts to agglomerate the fine mineral particles to lower the fines content of the bitumen-rich solvent phase.

[0009] Shelfantook et al. (Canadian Patent 1,293,465) discloses a bitumen froth treatment using a circuit comprising a plurality of serially connected mixer and inclined plate settler units. A light hydrocarbon diluent, such as naptha, moves counter-currently through the circuit so that as the bitumen content of the stream being settled diminishes, the concentration of diluent in that stream increases. A circuit consisting of three pairs of alternating mixers and settlers is reported as producing a bitumen product stream of the same order of purity and same order of recovery as obtained by dilution centrifuging. More specifically, the bitumen product stream in Table II reports a composition comprising 55.7% bitumen, 4.7% water, 0.7% solids, and 39.0% naptha.

[0010] Birkholz et al. (Canadian Patent 2,232,929) discloses a method for processing a diluted oil sand froth that contains hydrocarbons, water, clays and coarse solids and that is withdrawn from a lower part of a primary fluid separation vessel of a paraffinic solvent froth treatment unit. The method includes further diluting the underflow stream, agitating the underflow stream at a shear level sufficient to form agglomerates of asphaltenes and clays, and separating other hydrocarbons released into an upper fluid layer.

[0011] Tipman et al. (Canadian Patent 2,200,899) discloses a method for processing the underflow stream from a primary separation vessel of a paraffinic solvent froth treatment unit. Bitumen froth is mixed with a paraffinic diluent or solvent and fed to a primary

separation vessel. The method includes vigorously agitating the underflow from the primary separation vessel in an agitating tank at such a shear level that agglomerates of asphaltenes and clays are formed. The agglomerates are then separated out in a middlings stream from a secondary separation vessel.

[0012] Tipman et al. (Canadian Patent 2,353,109) discloses a solvent recovery unit used to treat the underflow stream from the last separation step in a paraffinic solvent process for separating bitumen from oil sands froth. The paraffinic solvent process relies upon the precipitation of asphaltenes to assist in the removal of water and solids from the froth. Consequently, the underflow stream from the paraffinic solvent process contains, among other things, water, solvent, solids, precipitated asphaltenes and other unrecovered hydrocarbons. However, the precipitated asphaltenes trap the light diluent in the underflow stream such that the underflow poses an environmental hazard and financial liability. A solvent recovery process is thus used to vaporize the solvent out of the underflow for recovery as an overhead vapor stream. While the use of a low boiling solvent makes the recovery easier, it also increases the operational risk of fire that can cause substantial damage.

[0013] Mishra et al. (U.S. Patent 6,019,888) discloses a bitumen froth treatment using a diluent and an ethoxylated nonylphenol surfactant with 4 to 13 ethoxyl groups. These surfactants have a molecular weight between 393 (4 ethoxyl groups) and 789 (13 ethoxyl groups) and are used at a ratio of between 1:10 (10 ppm) and 1:10,000 (1 wt%) kilograms of bitumen/diluent mix to milligram of surfactant. Optionally, anionic or cationic flocculants may also be used at between 1 ppm and 0.5 wt%.

[0014] Cymerman et al. (U.S. Patent 6,746,599) discloses that cleaned froth or "dilbit" should have less than 1.0% water and less than 0.3% solids before being processed in an upgrading facility. However, Cymerman explains that the ability to achieve a solution has been constrained by various factors including the affinity between clay and bitumen, the need to minimize bitumen losses in the tails or sludge, the diluent-to-bitumen ratio in the dilbit should not exceed 0.8, the equipment should be simple and inexpensive to

operate, and additives, such as demulsifiers, should be used only sparingly. Accordingly, Cymerman discloses dilution of bitumen froth with naphtha at a naphtha/bitumen ratio of 0.5:1 to 0.8:1 and delivering this "dilfroth" into a gravity settler vessel or "splitter." In one embodiment, Cymerman subjects the splitter dilbit to further treatment in a "polisher" vessel having a retention time of 5 to 24 hours. Optionally, a demulsifier is added to the splitter dilbit treated in the polisher to produce a polished dilbit overhead product having reduced water and solids. Example 1 shows that the water content could be reduced from 4.57% in the splitter overflow to 0.2% in the polisher overflow by allowing the dilbit to settle for 26 hours in the polisher vessel with 40 ppm demulsifier. Example 2 shows that a scrubber vessel fed with a 5:1 ratio of naphtha/bitumen could produce a scrubber underflow or tailings with about 1.75% bitumen.

[0015] Despite the development of these froth treatment processes, there remains a need for an improved froth treatment process that produces a diluted bitumen stream of higher quality, for example having less water, less solids, and less diluent. It would be desirable if this improved process would also increase bitumen recovery by reducing asphaltene losses in the tailings. It would be even further desirable if this improved process could be performed without requiring high solvent-to-bitumen ratios, long residence times or numerous or expensive processing units.

[0016] The present invention provides an improved froth treatment process that meets these needs. Unlike existing processes, the process of the present invention produces a diluted bitumen stream with low water content analogous to a paraffinic process, without requiring use of a paraffinic diluent, but enabling the use of various diluents or solvents. Furthermore, the invention may utilize a diluent-to-bitumen ratio of approximately 0.65, which is characteristic for the conventional naphtha-based process. The use of naphtha, or another solvent other than a paraffin, leads to improved bitumen recovery efficiency because asphaltene precipitation is largely avoided. The diluent-to-bitumen ratios used in the invention are lower than the required diluent-to-bitumen ratio of approximately 2.0 that is required for the paraffinic process for the precipitation of asphaltenes. The invention provides the unique and surprising result that a single process can provide the

simultaneous advantages of using any of a variety of hydrocarbon solvents, using a low diluent-to-bitumen ratio, and producing a diluted bitumen stream having low water content. Accordingly, the process of this invention yields exceptional product quality without the heretofore accompanying disadvantage of the low space/time yield associated with high solvent-to-bitumen ratios, nor the requirement of using only a paraffinic diluent as is dictated by the paraffinic froth treatment process.

#### SUMMARY OF THE INVENTION

[0017] The present invention provides methods of processing bitumen. A preferred method comprises diluting a bitumen source with a hydrocarbon diluent, contacting the bitumen with a zone settling aid, flocculating water and fine solids in the diluted bitumen, separating the flocculated water and fine solids from the solvent-diluted bitumen, and producing dry, clean diluted bitumen. Preferably, the diluted bitumen will have less than 2.0 wt% water and less than 0.5 wt% fine solids, but most preferably less than 0.7 wt% water and less than 0.2 wt% fine solids. The method may further comprise maintaining the diluted bitumen under conditions that avoid the precipitation of asphaltenes from the bitumen, preferably such that the dry, clean diluted bitumen comprises essentially all, such as greater than 96%, of the asphaltene content from the bitumen source. The hydrocarbon diluent is preferably selected from aliphatic hydrocarbons, aromatic hydrocarbons commercially available as naphtha, gasoline, natural gas condensate, paraffins, and combinations thereof. Furthermore, the step of contacting the bitumen with a zone settling aid may be performed upstream of or within a primary froth treatment vessel. In one embodiment, the bitumen source is bitumen froth from a hot water extraction process.

[0018] In another specific embodiment, the method further comprises passing the diluent counter-current to the water and fine solids. This counter-current flow may be performed in a series of zone settling stages. Optionally, the step of separating includes gravity settling.



[0019] In still another embodiment, the method further comprises aerating a slurry containing bitumen, water and inorganic solids to form a bitumen froth, and diluting the bitumen froth with a hydrocarbon diluent to produce the diluted bitumen. The method may be performed wherein the bitumen source is diluted to a diluent-to-bitumen ratio less than 1.

[0020] In a preferred embodiment, the zone settling aid comprises a polyoxyalkylate polymer having a molecular weight between about 2,000 and about 2,000,000. A suitable polyoxyalkylate polymer is a reaction product of a polyol and one or more alkoxide species. Optionally, the alkoxide species is selected from ethylene oxide, propylene oxide, glycidol, butylene oxide, epichlorohydrin and combinations thereof. Optionally, the polyol is sorbitol. An exemplary polyoxyalkylate polymer includes two or more block polymers selected from ethylene oxide, propylene oxide, and butylene oxide and epichlorohydrin. Glycidol would generally not form its own block, but may be advantageously included within a block or between blocks in order to provide branching.

[0021] In a more specific embodiment, the polyoxyalkylate polymer includes block polymers of propylene oxide and ethylene oxide. In yet another option, the propylene oxide block polymer has between 15 and 25 propylene oxide groups, and wherein the ethylene oxide block polymer has between 5 and 15 ethylene oxide groups per arm of a branched polymer. Optionally, the propylene oxide block polymer extends from the polyol, and the ethylene oxide block polymer extends from the propylene oxide block polymer. Optionally, the polymer comprises between 10% and 50% ethylene oxide depending on molecular weight and oxide composition, such as between 20% and 40% ethylene oxide preferably between 25% and 35% ethylene oxide or more preferably between 28% and 32% ethylene oxide. Most preferably, the polymer has a molecular weight between about 2,000 and about 2,000,000. At the higher end of this molecular weight range, say above, 1,000,000, it may be desirable to increase the EO content and degree of branching through incorporation of polyfunctional oxides such as glycidol or bis-epoxides to maintain desirable solubility characteristics and fluid rheological properties. Accordingly, the block polymers, especially those having a molecular weight

greater than 1,000,000, most preferably comprise between 10% and 50% ethylene oxide, such as between 25% and 40% ethylene oxide or between 28% and 35% ethylene oxide with a high degree of branching built into the molecular architecture.

[0022] The zone settling aid may be an alkoxylate polymer having the formula:  $\text{Acc} - [(\text{Ox}_1)_{\text{A}_1} - (\text{Ox}_2)_{\text{A}_2} - \dots (\text{Ox}_i)_{\text{A}_i}]_n$ , wherein Acc is an acceptor and  $\text{Ox}_1$  to  $\text{Ox}_i$  are oxide species, wherein each oxide is independently selected from ethylene oxide, propylene oxide, glycidol, butylene oxide, epichlorohydrin, and combinations thereof, wherein  $\text{A}_1$  to  $\text{A}_i$  is between 0 and 150,000, wherein  $n$  is between about 1 and 100, and wherein the molecular weight of the alkoxylate polymer is between about 1000 and about 2,000,000 g mole<sup>-1</sup>. Optional alkoxylate polymers may have a ratio of butylene oxide to propylene oxide between about 200:1 and about 1:200, a ratio of ethylene oxide to propylene oxide is between about 200:1 and about 1:200, or a ratio of butylene oxide to ethylene oxide is between about 200:1 and about 1:200. Preferably, the alkoxylate has a molecular weight between about 2000 and about 1,000,000. It is also preferred to add the alkoxylate polymer to a froth treatment system at a concentration of between about 1 wt. ppm and about 750 wt. ppm, such as between about 25 wt. ppm and about 300 wt. ppm.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0023] FIG. 1 is a flow diagram of a counter-current zone settling process for bitumen froth treatment.

[0024] FIG. 2 is a graph of the interface height as a function of time for each column of diluted bitumen that was treated with a zone settling aid in Example 1.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0025] The process of the present invention is suitable for treatment of any bitumen source. Examples of commercial significance include, without limitation, the Clark hot water process (CHWP) and low energy extraction (LEE) processes. In a preferred embodiment, the present invention is used to treat bitumen froth. As used herein,

reference to bitumen froth includes a primary froth, a secondary froth, any other froth containing bitumen, or a combined froth. Bitumen sources include, without limitation, oil sands, crude oil and oil shale.

[0026] The present invention provides a method of processing bitumen, wherein the bitumen is typically first diluted with a hydrocarbon diluent, preferably at a diluent-to-bitumen ratio of less than 1. The bitumen is contacted with a zone settling aid of the present invention for the purpose of removing water and fine solids in the diluted bitumen. Where the bitumen source is deaerated bitumen froth from an oil sand process, the bitumen is preferably contacted with a zone settling aid upstream of or within a primary froth treatment vessel. The water and fine solids can then be easily separated from the diluted bitumen to produce a dry, clean diluted bitumen stream, preferably having less than 1.0 wt% water and less than 0.5 wt% fine solids. Based on experience, 1wt% water is expected to be associated with 0.3 wt% solids.

[0027] In one embodiment of the invention, the method includes maintaining the diluted bitumen under conditions that avoid the precipitation of asphaltenes from the bitumen. In this manner, it is possible for the dry, clean diluted bitumen to comprise essentially all of the asphaltene content from the bitumen source, preferably greater than 96% of the asphaltene content, and more preferably greater than 99% of the asphaltene content.

[0028] A diluent is added to the bitumen froth to improve separation of water in the bitumen froth from the bitumen and diluent. A diluent, such as naphtha, serves to reduce the hydrocarbon phase viscosity and increase the density differential between the hydrocarbon phase and the water and solids phase (referred to as underflow). The diluent is preferably a hydrocarbon, including, without limitation, mixed refinery products such as naphtha, gasoline, diesel fuel, kerosene, and heating oil, or more refined products such as butane, pentane, hexane, heptane, octane, benzene, toluene or xylene or mixtures thereof. The preferred diluent is naphtha.

[0029] It is believed that the space/time yield of the process of this invention is only limited to a diluent-to-bitumen ratio that would provide a practical density difference to facilitate water separation under natural gravitational conditions. Preferably, the diluent-to-bitumen ratio is greater than or equal to 0.35. It should be recognized that the diluent-to-bitumen ratio may vary from a primary separation vessel to any secondary or tertiary separation vessel that may be used in the process. Accordingly, the diluent-to-bitumen ratio in a primary separation is preferably less than or equal to 1. If the process includes a secondary separation, then the diluent-to-bitumen ratio is preferably between 1 and 5. Further still, if the process includes a tertiary separation, then the diluent-to-bitumen ratio is preferably between 10 and 30. Embodiments of the process that include two or more separations will preferably involve a counter-current flow, such that the diluted bitumen from a later separation is input into the previous separation.

[0030] The separations are each carried out in a flotation tank or gravity separator designed to allow separation of a bitumen froth fraction from a water and solid fraction. Any commonly used unit processes in mineral processing may be used, for example a floatation tank, screens, inclined plate separator, hydraulic classifiers, hydrocyclone separators, centrifuges, and combinations of these units. The separations may also be carried out in multiple vessels and/or multiple vessel types, most preferably in series, that can accomplish a separation into at least two fractions, one fraction having much of the bitumen and the other fraction having much of the water and solids.

[0031] A preferred zone settling aid for use in the present invention comprises a polyoxyalkylate having the following form:  $\text{Acc} - [(\text{Ox}_1)_{\text{A1}} - (\text{Ox}_2)_{\text{A2}} - \dots (\text{Ox}_i)_{\text{Ai}}]_n$ , where  $\text{Ox}_1$  to  $\text{Ox}_i$  are different oxides, oxide blocks or mixed oxide blocks, and Acc is an acceptor. Each of the oxides  $\text{Ox}_1$  to  $\text{Ox}_i$  are selected from ethylene oxide (EO), propylene oxide (PO), butylene oxide (BO), epichlorohydrin (EPI) or mixed oxides, the mixed oxides being a mixture of EO, PO, glycidol, BO and/or and EPI. The EO:PO, EO:BO or PO:BO ratio may range from 200:1 to 1:200. The value of A1 to Ai may range between 0 and 150,000. The amount of EPI added is used to invoke incorporation of charge density through secondary reaction with nitrogen-based organic or other carbon-chloride

reactive reagents. The value of  $n$  represents the functionality. In certain embodiments, the polyoxyalkylates may be derivatized.

[0032] An acceptor for the oxyalkylation reaction is a chemical having one or more active hydrogen atoms that are easily substituted in an epoxide reaction. This category of chemical compounds includes any hydrogen atom that is connected to an element other than carbon. Examples of such acceptors are water, alcohols, polyalcohols such as glycerol, Sorbitol, pentaerythritol, sugars such as glucose, sucrose and cellulose, amines, such as ammonia, alkylamines, polyalkylpolyamines such as ethylene diamine, diethylene triamine, triethylene tetra amine, hexaethylene heptaamine, carboxylic and polycarboxylic acids, amids and polyamids, thiols and polythiols, alkylphenol formaldehyde resins and amine modified alkylphenol formaldehyde resins. The acceptors result in a polymer typically having a functionality of between 1 to about 100, but the functionality could be as high as 150,000 in the polymeric type acceptors.

[0033] Acceptors can thus be classified as material having an active hydrogen where an active hydrogen is defined as a hydrogen atom bonded to an element other than carbon. These include functional groups such as alcohols, carboxylic acids, amines, amides, thiols and can range from being mono-functional to polyfunctional. Specific examples of commercially significant acceptors are water, ethylene glycol, propylene glycol, glycerol, TMP, pentaerythritol, ammonia, alkyl and aryl amines, polyamines such as ethylene diamine, diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, pentaethylene hexamine, polyethylenimine, mono-, di-, tri and polycarboxylic acid derivatives, monosaccharides, disaccharides and polysaccharides such as glucose, sucrose and cellulose. In addition alkylphenolformaldehyde resins and amine modified alkylphenolformaldehyde resins are also useful as acceptors for producing zone settling aids.

[0034] Crosslinking agents may be utilized to increase the molecular weight of the polymer through crosslinking reactions. Suitable crosslinking agents include diepoxides, diacids, polyacids, polyacrylic acids, isocyanates leading to the formation of complex

polyesters, complex branched ethers and complex branched urethanes. Combinations of polyoxyalkylate polymers having different molecular architectures can be co-reacted either in sequence or as blends to produce complex crosslinked polymers involving reaction with poly-epoxides, polyacids and poly-isocyanates leading to the formation of complex polyoxyalkylate ethers, esters and urethanes. Glycidol is also a useful monomer to introduce branching in a propagating chain which can be used advantageously to optimize the molecular architecture specifically regarding molecular weight, fluid viscosity, interfacial activities and relative solubilities.

[0035] The resulting polymer that is useful as a zone settling aid has a molecular weight of between about 1000 and about 2,000,000, preferably between about 2000 and about 1,000,000.

[0036] The zone settling aid may be formulated with a carrier, such as kerosene, naphtha, hydrocarbon, or any other suitable diluent or diluent mixture, including, without limitation, water or methanol. The concentration of the carrier in the formulation may range from between 0 to about 99 wt. %.

[0037] A particularly preferred zone settling aid is a polyoxyalkylate polymer based on sorbitol. Such a polymer may be referred to as a "star polymer." The polyoxyalkylate polymer includes two or more block polymers selected from ethylene oxide, propylene oxide, and butylene oxide. Optionally, the polyoxyalkylate polymer includes block polymers of propylene oxide and ethylene oxide, for example where the propylene oxide block polymer has between 15 and 25 propylene oxide groups, and wherein the ethylene oxide block polymer has between 5 and 15 ethylene oxide groups. In one embodiment, the propylene oxide block polymer extends from the polyol, and wherein the ethylene oxide block polymer extends from the propylene oxide block polymer. Still further, the polymer may comprise between 10% and 50% ethylene oxide, between 20% and 40% ethylene oxide, between 25% and 35% ethylene oxide, or between 28% and 32% ethylene oxide. Suitably, these polymers preferably have a molecular weight between

about 1,000 and about 2,000,000. The exact makeup of the polymer determines the relative solubility of the polymer and its ability to settle and remove water and solids.

[0038] Now referring to FIG. 1, a flow diagram of a suitable counter-current zone settling process for bitumen froth treatment is shown. In a Clark Hot Water Process, a conditioned bitumen slurry 12 is fed into a primary separation vessel (PSV) 14. Bitumen becomes attached to air bubbles and forms a froth that exits the PSV in an overflow stream 16. The PSV will also typically produce a middlings stream 18 and an underflow or tailings stream 20, either or both of which may be further processed in a tailings oil recovery vessel (TORV) 22 to produce a secondary froth stream 24. Regardless of the exact content or processing scheme, a bitumen froth stream 26 is delivered for processing in a froth treatment system 28.

[0039] The froth treatment system 28, as shown, includes three zone settling vessels 30, 32, 34, that are operated with the water and solids 36 from the deaerated froth passing in counter-current flow to a hydrocarbon diluent, such as aliphatics, aromatics, naphtha, gasoline, natural gas condensate, and combinations thereof. A source of clean hydrocarbon diluent 38 is introduced into the third stage settling vessel 34. If desirable, the hydrocarbon diluent may be mixed in a mixing vessel 40 prior to entry into the vessel 34 to assure efficient contact between the hydrocarbon diluent and any bitumen remaining the tailings. Similar mixing vessels 40 may be used prior to the other settling vessels 30, 32.

[0040] In each of the vessels 30, 32, 34, the hydrocarbon diluted bitumen 42 is buoyant and rises to the top of the vessel to be withdrawn. At the same time, the water and solids 36 sink within the vessel to be withdrawn from the bottom. By passing the water and solids 36 successively from vessel 30 to vessel 32 to vessel 34, the tailings become more and more concentrated with less and less bitumen. By passing the hydrocarbon diluent from vessel 34 to vessel 32 to vessel 30, the bitumen content of the hydrocarbon increases and the overall bitumen recovery is maximized. While any number of vessels or stages may be used, three stages is generally sufficient. Finally, the tailings 44 are first

treated in a diluent recovery unit prior to being discarded and the dry and clean diluted bitumen stream 46 is transferred to a bitumen upgrading facility.

[0041] In accordance with the present invention, a zone settling aid is added to the froth treatment process. While the zone settling aid may be beneficially added at any one or more points in the process, the zone settling aid is preferably added to the primary froth treatment vessel 30, to mixer 40 just before the vessel 30, to the froth stream 26, or even to the diluted bitumen recycle stream being returned to vessel 30. The use of the zone settling aid improves separation efficiency of the water and solids out of the diluted bitumen. The improved separation results in greater overall bitumen recovery (especially greater asphaltene recovery), higher quality (drier and cleaner) diluted bitumen 46, greater processing rates through a given set of zone settling vessels, and lower bitumen content in the tallings 44. Other advantages of the process may become apparent over time through expanded use of the zone settling aids. It is foreseen that optimization of a zone settling aid may involve injection at any, or even each stage.

#### EXAMPLE 1

[0042] A bitumen froth containing approximately 60% bitumen, 30% water and 10% solids was mixed with a hydrocarbon diluent consisting of 30% toluene and 70% heptane to simulate naphtha. The diluent to bitumen ratio (D:B) of the diluted bitumen was 0.75 and the temperature of the mixture was 50°C.

[0043] A first zone settling aid (AST-3) was prepared from a polyethylene amine acceptor having on average nine active hydrogen atoms, a first propylene oxide block of about 1451 daltons per branch, and a second ethylene oxide block of about 435 daltons per branch. The resulting polyoxyalkylate has a molecular weight of about 17,000 daltons. The first zone settling aid was mixed with diluted bitumen at 50 ppm and 100 ppm concentrations, separately.

[0044] A second zone settling aid (AST-2) was prepared from a triol acceptor having three active hydrogen atoms that were used to prepare a sequential polymer having three branches. Each branch had a first propylene oxide block of about 3000 daltons, a 50/50



mixture of ethylene oxide and propylene oxide block of about 3000 daltons, and a third propylene oxide block of about 3000 daltons. This second zone settling aid was mixed with diluted bitumen at a 100 ppm concentration.

[0045] The mixture was then placed in a glass column where the height of an interface between the oil and tailing phases could be observed and measured. These phases were allowed to settle for 25 minutes to determine a settling rate and the water content of the hydrocarbon phase. The water content in a blank of the diluted bitumen was about 3.95 % throughout the column with no detectable settling over a period of 25 minutes. The dry, clean diluted bitumen contained 0.34% water when treated with 100 ppm of the first zone settling aid, 0.58% water when treated with 50 ppm of the first zone settling aid, and 0.60% water when treated with 50 ppm of the second zone settling aid. The water content as a function of fluid level is provided in Table 1.

[0046] Table 1. Effects of chemical addition on dehydration at three levels of fluid

	Blank	AST-3	AST-3	AST-2
Chemical dosage (ppm)	0	50	100	50
KF. H <sub>2</sub> O%				
Oil phase	3.95	0.58	0.34	0.598
160 mm from the bottom	3.65	0.65	14.6	0.582
80 mm from the bottom	3.9	36.42	15.2	41.3

[0047] Upon placing the mixtures into columns, the initial interface heights were between 300 and 350 mm. Figure 2 was prepared by measuring the interface height of each column over a 25 minute period. As shown, the interface of the blank was unchanged. The first zone settling aid (AST-3) brought about a 12.6 mm/min drop of the interface with a 50 ppm addition and 5.6 mm/min drop with a 100 ppm addition, while the second zone settling aid (AST-2) brought about a settling rate similar to the 50 ppm addition of the first zone settling aid (AST-3).

#### EXAMPLE 2

[0048] A zone settling aid according to the invention was prepared with a sorbitol acceptor having six active hydrogen atoms, a first PO block of about 1000 daltons for

each of the six branches, and a second EO block of about 300 daltons per branch. The total molecular weight of the zone settling aid was about 7,800 daltons.

[0049] A 404 gram sample of bitumen froth was 60% bitumen (246 grams bitumen), 30% water and 10% solids. The froth was heated to 85°C and stirred for three minute to homogenize the sample. To achieve a diluent:bitumen ratio of 0.65, about 160 grams of naphtha was heated to 85°C and added to the froth with stirring for two minutes at 1000 RPM with a paint stirrer. Then, 0.57 ml of a 10% solution of the zone settling aid was added to the diluted bitumen with three minutes of stirring. Upon settling, about 300 grams of dry, diluted bitumen was removed from the top of the settler for a recovery of about 182 grams of bitumen. The diluted bitumen had a water content of 0.608% determined by Karl Fischer titration.

[0050] A second stage settler was simulated by adding back 118 grams of naphtha to the underflow remaining in the bottom of the vessel with stirring for 3 minutes. It was determined that 69 grams bitumen was in the second stage vessel with 446 grams naphtha for D:B ratio of about 2.47. Upon settling, about 200 grams of dry, diluted bitumen was removed from the top of the second stage settler and determined to contain about 58 grams of bitumen. Accordingly, the first and second stages recovered about 97.3% of the available bitumen.

[0051] A third stage settler was simulated by adding 142 grams naphtha to the remaining underflow. This provided a D:B ratio of about 24 in the third stage.

[0052] The terms "comprising," "including," and "having," as used in the claims and specification herein, shall be considered as indicating an open group that may include other elements not specified. The term "consisting essentially of," as used in the claims and specification herein, shall be considered as indicating a partially open group that may include other elements not specified, so long as those other elements do not materially alter the basic and novel characteristics of the claimed invention. The terms "a," "an," and the singular forms of words shall be taken to include the plural form of the same words, such that the terms mean that one or more of something is provided. For example,

the phrase "a solution comprising a phosphorus-containing compound" should be read to describe a solution having one or more phosphorus-containing compound. The term "one" or "single" shall be used to indicate that one and only one of something is intended. Similarly, other specific integer values, such as "two," are used when a specific number of things is intended. The terms "preferably," "preferred," "prefer," "optionally," "may," and similar terms are used to indicate that an item, condition or step being referred to is an optional (not required) feature of the invention.

[0053] It will be understood from the foregoing description that various modifications and changes may be made in the preferred embodiment of the present invention without departing from its true spirit. It is intended that this description is for purposes of illustration only and should not be construed in a limiting sense. The scope of this invention should be limited only by the language of the following claims.

## CLAIMS

What is claimed is:

1. A method of processing bitumen, comprising:  
diluting a bitumen source with a hydrocarbon diluent to a diluent-to-bitumen ratio of less than 1;  
contacting the bitumen with a zone settling aid;  
• flocculating water and fine solids in the diluted bitumen;  
separating the flocculated water and fine solids from the diluted bitumen; and  
producing a dry, clean diluted bitumen having less than 1.0 wt% water and less than 0.5 wt% fine solids.
2. The method of claim 1, wherein the diluted bitumen has less than 0.7 wt% water and less than 0.3 wt% fine solids.
3. The method of claim 1, further comprising:  
maintaining the diluted bitumen under conditions that avoid the precipitation of asphaltenes from the bitumen.
4. The method of claim 3, wherein the dry, clean diluted bitumen comprises essentially all of the asphaltene content from the bitumen source.
5. The method of claim 1, wherein the step of contacting the bitumen with a zone settling aid is performed upstream or within a primary froth treatment vessel.
6. The method of claim 1, wherein the bitumen source is deaerated bitumen froth.
7. The method of claim 1, wherein the bitumen source is diluted to a diluent-to-bitumen ratio less than 0.75.

8. The method of claim 1, further comprising:  
passing the diluent counter-current to the water and fine solids.
9. The method of claim 8, wherein the counter-current flow is performed in a series of zone settling stages.
10. The method of claim 1, wherein the step of separating includes gravity settling.
11. The method of claim 1, further comprising:  
aerating a slurry containing bitumen, water and inorganic solids to form a bitumen froth; and  
diluting the bitumen froth with a hydrocarbon diluent to produce the diluted bitumen.
12. The method of claim 1, wherein the zone settling aid comprises a polyoxyalkylate polymer having a molecular weight between about 1,000 and about 2,000,000
13. The method of claim 12, wherein the polyoxyalkylate polymer is a reaction product of an acceptor and one or more alkyloxide species.
14. The method of claim 13, wherein the alkyloxide species is selected from ethylene oxide, propylene oxide, glycidol, butylene oxide, epichlorohydrin and combinations thereof.
15. The method of claim 13, wherein the acceptor is material having one or more active hydrogen atoms towards the oxyalkylation reaction.
16. The method of claim 13, wherein the acceptor is Sorbitol.

17. The method of claim 13, wherein the polyoxyalkylate polymer includes two or more block polymers selected from ethylene oxide, propylene oxide, and butylene oxide and epichlorohydrin.

18. The method of claim 13, wherein the polyoxyalkylate polymer includes block polymers of propylene oxide and ethylene oxide.

19. The method of claim 18, wherein the propylene oxide block polymer has between 15 and 25 propylene oxide groups, and wherein the ethylene oxide block polymer has between 5 and 15 ethylene oxide groups per arm of a branched polymer.

20. The method of claim 19, wherein the propylene oxide block polymer extends from the polyol, and wherein the ethylene oxide block polymer extends from the propylene oxide block polymer.

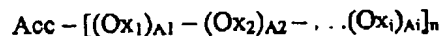
21. The method of claim 18, wherein the polymer comprises between 10% and 50% ethylene oxide.

22. The method of claim 18, wherein the polymer comprises between 20% and 40% ethylene oxide.

23. The method of claim 18, wherein the polymer comprises between 28% and 35% ethylene oxide.

24. The method of claim 21, wherein the polymer has a molecular weight between about 2,000 and about 2,000,000.

25. The method of claim 1, wherein the zone settling aid is an alkoxyate polymer having the formula:



wherein: Acc is an acceptor;

$Ox_1$  to  $Ox_i$  are oxides, wherein each oxide is independently selected from ethylene oxide, propylene oxide, glycidol, butylene oxide, epichlorohydrin, and mixtures thereof, wherein  $A1$  to  $Ai$  is between 0 and 150,000, wherein  $n$  is between about 1 and 100, and wherein the molecular weight of the alkoxyate is between about 1000 and about 2,000,000 g mole<sup>-1</sup>.

26. The method of claim 25, wherein the ratio of butylene oxide to propylene oxide is between about 200:1 and about 1:200.

27. The method of claim 25, wherein the ratio of ethylene oxide to propylene oxide is between about 200:1 and about 1:200.

28. The method of claim 25, wherein the ratio of butylene oxide to ethylene oxide is between about 200:1 and about 1:200.

29. The method of claim 25, wherein the alkoxyate has a molecular weight between about 2000 and about 1,000,000.

30. The method of claim 25, wherein the alkoxyate is added to the system at a concentration of between about 1 wt. ppm and about 750 wt. ppm.

31. The method of claim 25, wherein the alkoxyate is added to the system at a concentration of between about 25 wt. ppm and about 300 wt. ppm.

32. The method of claim 1, wherein the hydrocarbon diluent comprises naphtha.

33. The method of claim 1, wherein the hydrocarbon diluent is selected from aliphatics, aromatics, naphtha, gasoline, natural gas condensate, paraffins, and combinations thereof.

34. The method of claim 13, wherein the acceptor is a low molecular weight polyethyleneimine having a functionality range from about 4 to 14 active hydrogen atoms per molecule.



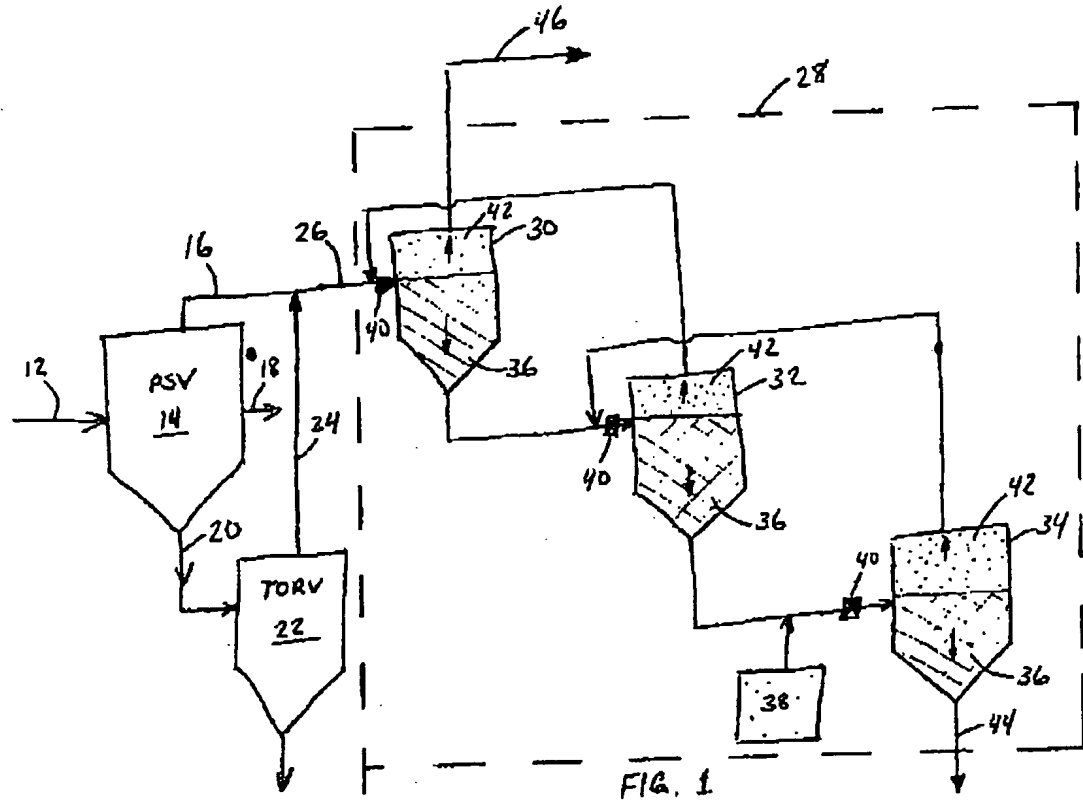


Figure 2. Effects of chemical addition on settling rate

